



# The energy transfer based fluorescent approach to detect the formation of silica supported phosphatidylcholine and phosphatidylserine containing bilayers

Alsu R. Mukhametshina<sup>b</sup>, Asiya R. Mustafina<sup>a,\*</sup>, Nikolay A. Davydov<sup>a</sup>, Irek R. Nizameev<sup>a</sup>, Marsil K. Kadirov<sup>a</sup>, Valery V. Gorbachuk<sup>b</sup>, Alexander I. Konovalov<sup>a</sup>

<sup>a</sup> A.E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov Str. 8, 420088 Kazan, Russia

<sup>b</sup> Kazan Federal University, Kremlevskaya Str. 18, 420008 Kazan, Russia



## ARTICLE INFO

### Article history:

Received 11 September 2013

Received in revised form

12 November 2013

Accepted 15 November 2013

Available online 23 November 2013

### Keywords:

Tb(III) complexes

Luminescence

Energy transfer

Phospholipid

Silica nanoparticles

## ABSTRACT

The work introduces the quenching of silica coated Tb(III) complexes by merocyanine 540 (MC540) and copper ions as a tool to reveal the adsorption of phosphatidylcholine (PC) and phosphatidylserine (PS) at various PS:PC ratio onto silica nanoparticles doped with Tb(III) complex. The binding of MC540 with PC-based bilayers and copper ions with PS-based ones are the basis of their use as organic and inorganic probes to sense PS:PC ratio in silica supported mixed bilayers. The enrichment of mixed bilayers with PS results in the displacement of MC540 anions, while it enhances the binding with copper ions. The displacement or binding of probe ions results in the diverse luminescence response of Tb(III)-centred luminescence. The reestablishment of the steady state and time resolved luminescence is observed, when MC540 anions are applied as probes. The use of copper ions as probes results in the opposite quenching effect. The developed route enables to discriminate the formation of the phospholipids bilayers onto silica surface from those in the bulk of solution under various concentration conditions.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The aggregates of phospholipids (PhLs) have gained a great interest in recent decades as potential drug delivery systems [1–3], as capsules for hazardous luminescent or magnetic nanoparticles [4–7] and for mimicking the cell membrane properties [8–14]. The PhLs bilayers deposited onto silica beads or so-called supported lipid bilayers (SLB) [8–10] are of great importance for both mimicking processes taking part in cell membranes [13] or in growing the blood compatibility of nanomaterial for imaging and drug delivery [11,12]. The widespread application of SLB as mimics of cell membranes prompts great number of works concerning the regularities and conditions of their formation onto silica nanoparticles [14–20]. A number of methods have been applied to probe into the formation of SLB. The electrokinetic potential, surface pressure and adsorption isotherm measurements, atomic force microscopy, Cryo TEM imaging and contact angle measurements are applied to highlight both driving forces and optimal conditions of the SLB formation [14–20]. Nevertheless the development of the procedure to sense the deposition of various PhLs bilayers onto silica

beads is rather appealing task. The present work is inspired by the idea to apply donor → acceptor energy transfer as a basis of novel methodological approach to sense a formation of SLBs and to gain deeper insight into their binding and inclusion capacities. Our previous works highlight the effect of the adsorption and aggregation of cationic surfactants at the silica/water interface on the energy transfer from Tb(III) complexes coated by silica to the quenching molecules [21,22]. This procedure is based on the switching from the significant quenching of Tb(III)-centred luminescence when quenching molecules are located at the interface of Tb(III)-doped silica nanoparticles (SNs) to the reestablishment of the luminescence through the displacement of quenching molecules from the interface to the bulk of solution. The present work introduces Tb(III)-doped luminescent SNs as luminescent templates for the adsorption of PhLs and the energy transfer from Tb(III) to energy acceptors at the silica/water interface as the tool to reveal the deposition of PhLs bilayers onto SNs. The silica supported mixed bilayers based on zwitter-ionic phosphatidylcholine (PC, Scheme 1) and anionic phosphatidylserine (PS, Scheme 1) are of particular importance due to the mimicking of the cell apoptosis [23,24]. The works [16,17,25,26] highlight the enhanced affinity of cationic and zwitter-ionic phospholipids to negatively charged SNs. The choice of dye anions as quenchers of Tb(III)-centred luminescence is conditioned by the energy transfer from <sup>5</sup>D<sub>4</sub> of Tb(III) to the low

\* Corresponding author. Tel.: +7 843 2 727394; fax: +7 843 2 732253.  
E-mail addresses: [asiyamust@mail.ru](mailto:asiyamust@mail.ru), [asiya@iopc.ru](mailto:asiya@iopc.ru) (A.R. Mustafina).